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| A new series of water-soluble conjugated aromatic polyimines containing sulfonate groups have been synthesized via polycondensation reaction between diamines and dialdehydes at room temperature. The polymers are soluble in water and <i>N,N</i> -dimethylformamide (DMF), giving colored solutions with absorption maxima (λ_{max}) ranging from 400 to 480nm. One of the polyimines (PIP) showed strong fluorescence in aqueous solution and concentration dependence of photoluminescence has been investigated. Electrostatic self-assembly of multilayer films consisting of each polyimine as a polyanion and poly(diallyldimethylammonium chloride) as a polycation was successfully carried out by alternate deposition in corresponding aqueous solutions. | | | |
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Synthesis and self-assembled multilayer thin film formation of water-soluble conjugated aromatic polyimines

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SUMMARY:

A new series of water-soluble conjugated aromatic polyimines containing sulfonate groups have been synthesized via polycondensation reaction between diamines and dialdehydes at room temperature. The polymers are soluble in water and *N,N*-dimethylformamide (DMF), giving colored solutions with absorption maxima (λ_{max}) ranging from 400 to 480nm. One of the polyimines (**PIP**) showed strong fluorescence in aqueous solution and concentration dependence of photoluminescence has been investigated. Electrostatic self-assembly of multilayer films consisting of each polyimine as a polyanion and poly(diallyldimethylammonium chloride) as a polycation was successfully carried out by alternate deposition in corresponding aqueous solutions.

Introduction

Research interest in the synthesis and application of conjugated polymers due to the substantial π -electron delocalization along their backbones with useful electronic, optoelectronic, and photonic properties has significantly increased during the last two decades 1-4). Polymers with π -conjugated systems containing alternating carbon-carbon double and single bonds, which includes polyacetylene, poly(*p*-phenylene) (PPP), and poly(*p*-phenylene vinylene) (PPV) are of considerable importance⁵⁻⁷). Numerous reports on the electronic⁸⁻¹⁰, electrochemical, linear optical⁸⁻¹³, and nonlinear optical properties¹²⁻¹⁴ of these materials have been extensively reported so far. These properties may lead to practical applications such as information storage, optical signal processing, and materials for solar energy conversion⁴). Electroluminescence (EL) from conjugated polymers is another topic that has generated a lot of interest since the report of PPV based EL devices⁵.

One class of π -conjugated polymers that is less studied with respect to their electronic, optical, and nonlinear optical properties is the aromatic polyimines also known as polyazomethines or poly(Schiff bases)¹⁴⁻²⁴). The introduction of nitrogen atoms into the conjugated structure is another attempt to investigate the electronic and optical properties of these materials because the CH=N group is isoelectronic with the CH=CH group²⁵⁻²⁹). Their synthesis^{18,30}, excellent thermal stability^{17,31}, good mechanical strength and fiber-forming properties^{30,31}, thermotropic and lyotropic liquid crystal properties³⁰⁻³², and semiconducting properties of long alkoxy derivatives²¹ of the conjugated aromatic polyimines have been investigated in detail for many years. While it was recognized that the nitrogen in the polyimine backbone induced novel features and chemical flexibility like

polyaniline and unlike PPV, the infusibility and insolubility of conjugated aromatic polyimines in common organic solvents prevented their further investigation. Some reports have recently been made improving the poor processability of conjugated polyimines through changes in polymer structure^{21,22}). Soluble polyimines were also prepared by means of the reversible Lewis acid-base complexation^{25,26}).

Ultrathin organic films are currently gaining widespread interest because of the potential applications in integrated optics, sensors, and friction reducing coatings³³). Recently a new thin film fabrication technique based on the alternating adsorption of molecular layers of oppositely charged polymers (anionic and cationic polyelectrolytes) has been successfully applied to manipulate a wide variety of electroactive materials including conjugated polymers³⁴⁻³⁸). Multilayer thin films can be fabricated by simply alternating the dipping process between a polycation solution and a polyanion solution. With this processing approach in mind we have introduced sulfonate groups into the polyimine backbone expecting to induce flexibility and hydrophilicity to polymer chains and to be used as polyanions in the layer-by-layer deposition process. There have been many reports on the incorporation of sulfonic acid groups or sulfonate groups into polymer backbones such as poly(arylene ether)³⁹, polyamide⁴⁰, polyester^{41,42}, and poly(phenylene sulfide)⁴³. They showed various interesting properties such as better solubility, hydrogel formation, lyotropic liquid crystal behavior, and thermostable proton-conducting properties.

Here we report the synthesis of a new series of conjugated aromatic polyimines containing sulfonate groups in their backbone by means of polycondensation reaction between dialdehydes and diamines. The polyimines synthesized were soluble in water and used as anionic polyelectrolytes to fabricate

thin films by means of layer-by-layer deposition process driven by the ionic attractions developed between negatively and positively charged polyelectrolytes. The preparation, characterization, and self-assembled multilayer fabrication of the newly synthesized polyimines are described in detail.

Experimental part

Materials and reagents

4,4'-diaminostilbene-2,2'-disulfonic acid was purchased from Fisher Scientific Co. and used as received. 2,5-Diaminobenzenesulfonic acid was supplied by Aldrich and purified by recrystallization method in water. Terephthalidicarboxaldehyde and 2,5-thiophenedicarboxaldehyde were used without further purification (all from Aldrich). All the chemicals were used without further purification unless otherwise specified.

Polymer synthesis

The polymer synthesis is shown in Scheme 1. Polyimines were prepared via low temperature interfacial polymerization under vigorous agitation.

SIP Sodium hydroxide (0.21g, 5.30mmol) and 20ml of distilled water were placed in a 20ml flask equipped with a nitrogen inlet. 0.98g (2.65mmol) of 4,4'-diaminostilbene-2,2'-disulfonic acid was added while stirring and the pH of the solution was adjusted to 7 by adding small amount of dilute sodium hydroxide solution or the diamine compound. To this, terephthalidicarboxaldehyde (0.36g, 2.70mmol) in 20ml of chloroform was added all at once followed by addition of 0.14g (0.45mmol) of benzyltributylammonium chloride dissolved in 1ml water, and the

mixture was stirred vigorously. After the color changed from pale yellow to red, precipitates formed. Vigorous agitation was maintained at room temperature for 3hr. The mixture was then poured into 250ml ethanol and the solid was filtered. The solid product was washed with ethanol, a mixture of ethanol-water (2:1, v/v%), ethanol, and dried in vacuum oven at 85°C for 24hr. The polymer obtained was a dark red powder (1.09g, 80% yield).

IR (KBr) : 1619 (s; imine C=N) and 1202cm⁻¹ (s; sulfonic acid salt). ¹H NMR (DMSO) : δ 10.13 (Ar-N=CH) ; 8.80, 8.13, 7.80 (phenylene) ; 6.68 (vinylene).

Other polyimines were synthesized according to the same procedure with corresponding diamines and corresponding dialdehydes and were purified as described above.

SIT Monomer used were 4,4'-diaminostilbene-2,2'-disulfonic acid (0.83g, 2.25mmol) and 2,5-thiophene dicarboxaldehyde (0.32g, 2.30mmol), affording dark red powdery polymer (1.09g, 93% yield). IR (KBr) : 1618 (s; imine C=N) and 1196cm⁻¹ (s; sulfonic acid salt). ¹H NMR (DMSO) : δ 10.05 (Ar-N=CH) ; 8.95, 8.15, 7.80, 7.40 (phenylene and thiophene) ; 6.58 (vinylene).

PIP Polymer was obtained via polycondensation reaction between 2,5-diaminobenzenesulfonic acid (1.04g, 5.50mmol) and terephthaliccarboxaldehyde (0.75g, 5.60mmol). The product was a greenish yellow powder (1.55g, 95% yield). IR (KBr) : 1619 (s; imine C=N) and 1199cm⁻¹ (s; sulfonic acid salt). ¹H NMR (DMSO) : δ 10.10 (Ar-N=CH) ; 8.70, 8.05, 7.62, 7.20 (phenylene).

PIT Monomers, 4,4'-diaminostilbene-2,2'-disulfonic acid (0.94g, 5.00mmol) and 2,5-thiophene dicarboxaldehyde (0.71g, 5.10mmol) were used to obtain a yellow powder (1.44g, 95% yield). IR (KBr) : 1618 (s; imine C=N) and 1196cm⁻¹ (s; sulfonic acid salt).

¹H NMR (DMSO) : δ 10.01 (Ar-N=CH) ; 8.80, 8.10, 7.65, 7.35 (phenylene and thiophene).

Characterization

Infrared spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrometer using KBr pellet. Absorption spectra were taken from a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer. ¹H NMR spectra were taken on a Bruker ARX-250 spectrometer operating at 250MHz. Emission and excitation spectra were measured with SLM-AMINCO Model 8100 spectrofluorometer using aqueous solution of each polymer with known concentration. Differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) were obtained from a Du Pont Thermal Analyzer Model 2000 equipped with a Model 2910 DSC and a Model 2950 TGA under a nitrogen atmosphere with heating rates of 10 (DSC) and 20°C/min (TGA). The molecular weights of the polymers were determined by gel permeation chromatography (GPC) instrument (Waters Model 510 pump and Waters 410 refractive index detector) with styragel columns relative to polystyrene standards using DMF as an eluent.

Thin film fabrication through self-assembled layer-by-layer deposition

The formation of self-assembled multilayers of polyimines was carried out by using an aqueous solution of each polyimine with a concentration of 3mM (Ultrapure Millipore water was used.). Mutilayer formation was accomplished by using suitable polycation (poly(diallyldimethylammonium chloride), PDAC) since the sulfonate groups in the polyimine backbone were negatively charged in water. A solution of PDAC was prepared by diluting a 20wt% aqueous solution of PDAC (Aldrich) with

Millipore water. The final concentration was 3mM.. The multilayer fabrication process was employed according to the literature method³⁵⁻³⁷). The fabrication of layer-by-layer multilayer films is described as follows. A glass substrate with a negatively charged surface is immersed in the aqueous solution containing the cationic polyelectrolyte (PDAC) and then a monolayer of the polycation is adsorbed onto the glass surface. After thorough rinsing in Millipore water the glass substrate is immersed in the solution containing the anionic polyelectrolyte (polyimine). Again a monolayer of the polyanion is adsorbed. By repeating these steps in a cycle, alternating self-assembled layers of both polymers (PDAC and each polyimine) forming a multilayer film was obtained. After the film fabrication all the samples were dried overnight in air and then overnight in a vacuum oven at 50-60°C.

Results and discussion

The solubility of diamine monomers (4,4'-diaminostilbene-2,2'-disulfonic acid and 2,5-diaminobenzenesulfonic acid) in organic solvents commonly used in solution polymerization reaction such as DMF and N--methyl pyrrolidone (NMP) is very low and they have limited solubility in water as well. We, therefore, conjectured the conversion of sulfonic acid groups in the diamine monomers into sodium sulfonate groups by using equimolar amount of base. Finally the diamine monomers with sodium sulfonate groups were dissolved in water in the presence of a base (Sodium hydroxide was used in this experiment.) and reacted with a dialdehyde dissolved in chloroform to accomplish interfacial polycondensation reaction. Benzyltributylammonium chloride as a phase transfer catalyst (PTC) was used to increase the rate of polymerization⁴¹). We carried out the same polymerization

without PTC and found that the effect of the presence of PTC on the rate of polymerization and the molecular weights of the polymer was negligible. Precipitation was observed after mixing of two monomers and they remained as a fine suspension during the polymerization. Owing to the precipitation of the product polymer we thought that this phenomenon, heterogeneous polymerization system resulted in the relatively low molecular weights of **PIP** and **PIT** as shown in Table 1. The workup of these polymers was also difficult because they are soluble in water. Mixture of ethanol and water was used to wash the PTC and unreacted monomers out from the polymer.

We found that four polyimines as synthesized were soluble in water, DMF, and *N,N*--dimethyl acetamide (DMAc) according to the solubility tests. We were convinced that the sulfonate groups played an important role in improving solubility in above solvents. The GPC measurement of each polymer was performed in DMF solution. The results are shown in Table 1. For **SIP** and **SIT**, the molecular weights are relatively high compared to those of **PIP** and **PIT**. Distributions of the molecular weights seem to be uniform from the results of polydispersity. FT-IR spectra of the polymers showed characteristic bands of the functional groups expected such as imine group ($C=N$) near at 1620cm^{-1} and sulfonic acid salt near at 1120cm^{-1} ⁴⁴). DSC and TGA were performed on the polyimines. Incorporation of the sulfonate pendant groups disrupts chain packing and the resulting polymers were found to be amorphous⁴⁵). No melting peak was observed in the DSC thermogram. The polyimines showed high decomposition temperatures (T_d) as shown in Table 1. In the TGA data, **SIP** and **PIP** showed two thermal degradation respectively. According to a recent report⁴³⁾ the initial decomposition corresponds to the loss of the sulfonic acid group and the second thermal degradation are attributed to

polymer backbone degradation. In the case of polyimines with thiophene units; **SIT** and **PIT**, however, it seems that the both decomposition of sulfonate groups and polymer backbone occurred simultaneously.

Table 2 shows the absorption and fluorescence maxima of the polymer solutions in water. The emission maxima were obtained from excitation of the polymer solutions at their absorption maxima respectively. We, however, could not observe fluorescence from **SIP** and **SIT** solutions excited at each absorption maximum. But when excited at lower wavelengths (lower than 350nm), high intensity of fluorescence was observed from both the solutions. This fluorescence did not result from the conjugated polymer backbone but is thought to result from the low molecular weight fractions in the polymer. Fig. 1 shows the effect of concentration of each polymer in water on the fluorescence intensity. It is clearly seen that **PIP** has much stronger fluorescence than **PIT** in water. Both curves reveal the existence of an optimum concentration for the highest emission intensity. Above that point, fluorescence intensity decreases with increasing concentration as shown in Fig.1, which is a general case⁴²⁾.

We could fabricate alternating layers onto glass slides with four polyimines containing sulfonate groups as polyanions and PDAC as a polycation, respectively. By UV-VIS spectroscopy, it is demonstrated that the consecutive adsorption of layers is consistent and uniform as shown in Fig. 2 (for **SIP**). Fig. 3 depicts the electronic absorption of the conjugated polymer multilayer films at each λ_{max} (411nm for **SIP**; 433nm for **SIT**; 413nm **PIP**; 441nm for **PIT**) upto 5 bilayers. The absorption at each λ_{max} of the polymer is due to the $\pi-\pi^*$ transition of the conjugated chains of polyimine created within the assembled multilayer. As shown in Fig. 3, there is a linear relationship between the number of bilayers deposited and the absorbance of

the multilayer film upto 5 bilayers. It was found that each bilayer makes an equal and reproducible contribution to the absorbance of the assembled multilayer films. It has been established that monolayer adsorption depends on the condition of the polyelectrolyte solutions; especially concentration, temperature, and pH of the solution. It is generally accepted that for well defined multilayers the absorbance has a linear relationship with the number of bilayers and thickness of the films³⁵⁻³⁸⁾.

Conclusion

We are reporting, for the first time, the synthesis via interfacial polycondensation reaction and the characterization of specially designed series of conjugated aromatic polyimines containing sulfonate groups in their backbones. Due to the presence of sulfonate groups in the polymer backbones, they showed much improved solubility in water and DMF. The polyimines showed different absorption maxima (400-480nm) in water according to the molecular backbone structures. Among the polymers PIP showed the highest intensity of fluorescence in aqueous solution. We also demonstrated the fabrication of optical quality multilayer thin films of anionic (polyimine) and cationic (PDAC) polyelectrolytes on glass slides. The self-assembled films are fabricated by alternate adsorption from both polyelectrolyte aqueous solutions. Absorbances in the UV spectra were increased linearly with the number of adsorption step, implying that the spontaneous adsorption of the polyimines containing sulfonate groups and cationic polyelectrolytes was uniform and a result of ionic interactions.

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Figure captions and table legends

Scheme 1 Polymer synthesis

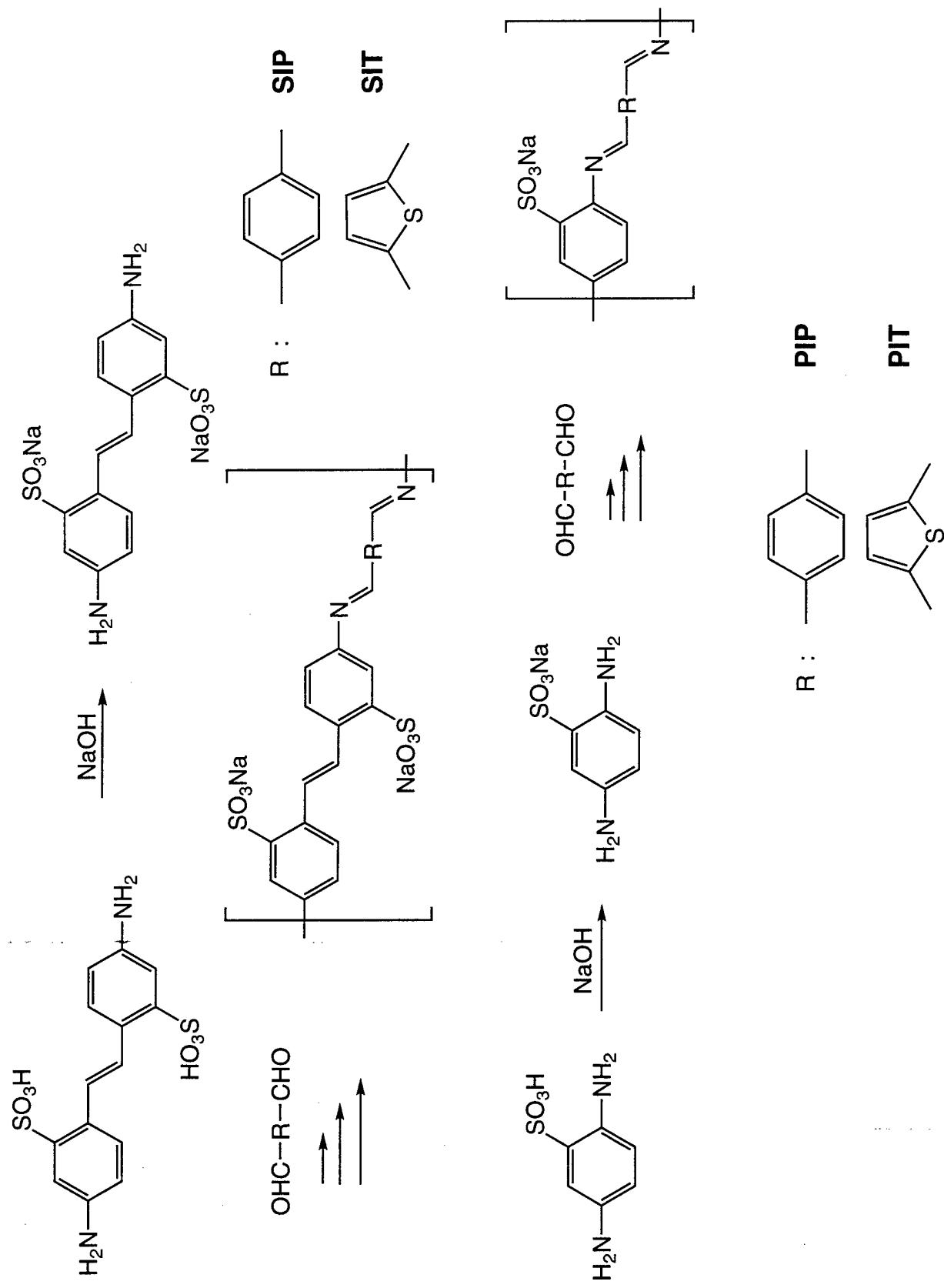
Fig. 1. Dependence of the concentration of the polymer solutions on the fluorescence intensity.

Fig. 2. Absorption spectra of SIP multilayer thin films with an increasing number of bilayers (1, 2, 3, 4, and 5 bilayers).

Fig. 3. Fabrication of assembled multilayer films of (a) SIP, (b) SIT, (c) PIP, and (d) PIT with PDAC.

Table 1. Properties of the polymers

Table 2. Absorption and fluorescence maxima of the polymers in water



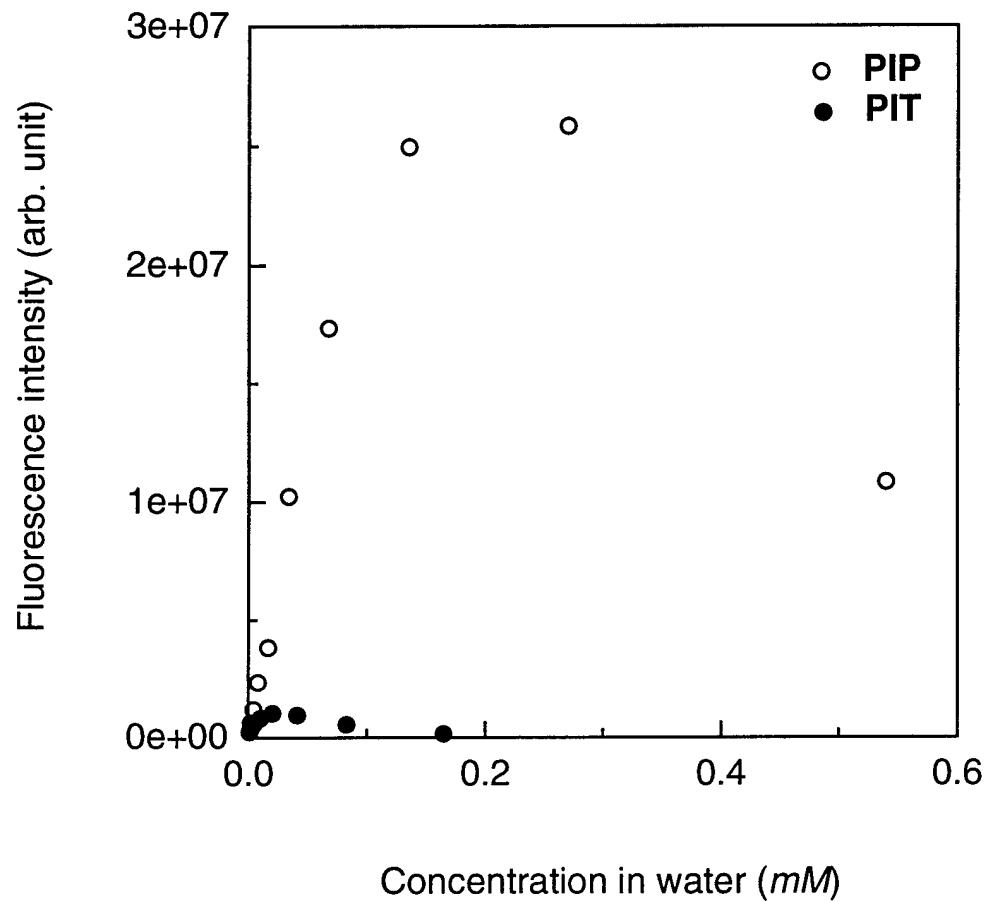


Fig. 1

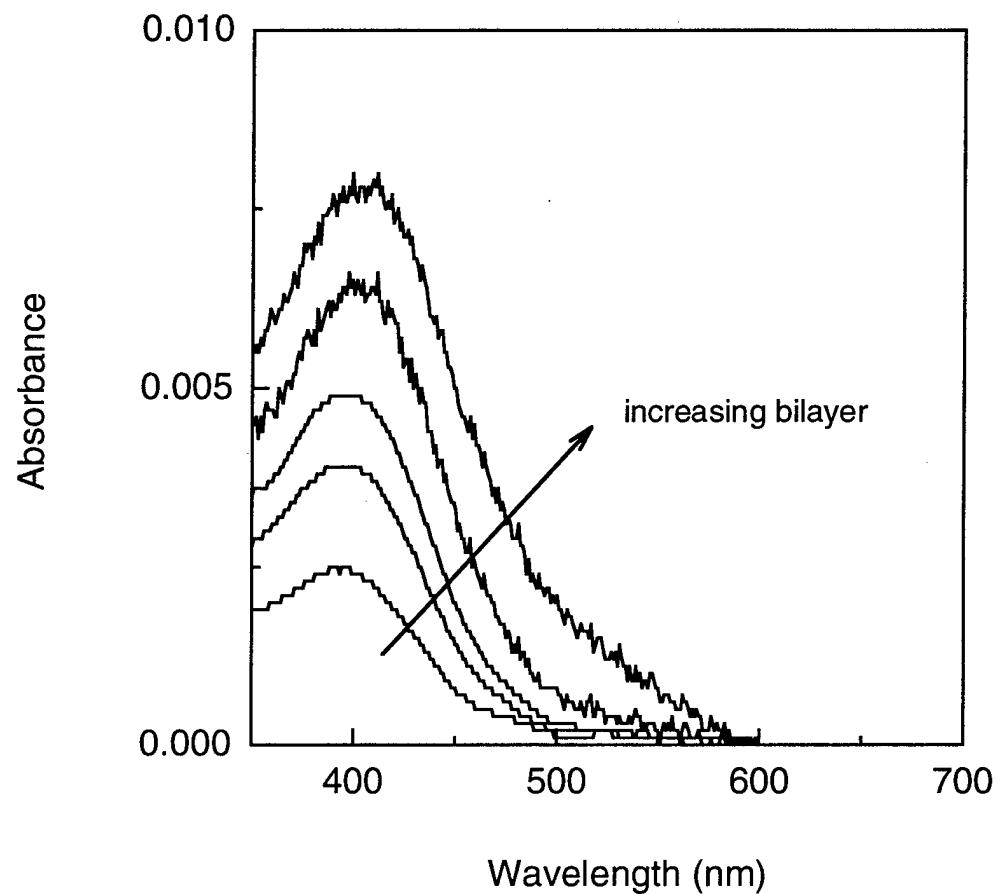
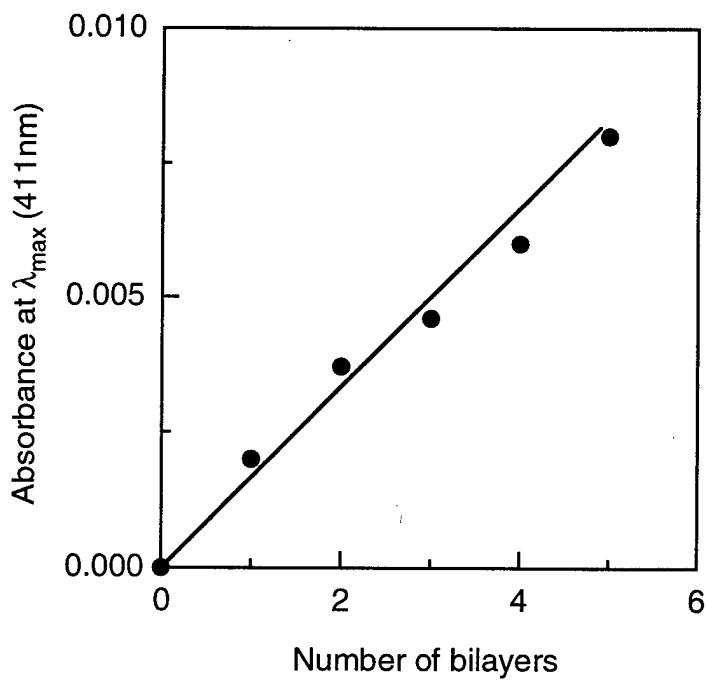
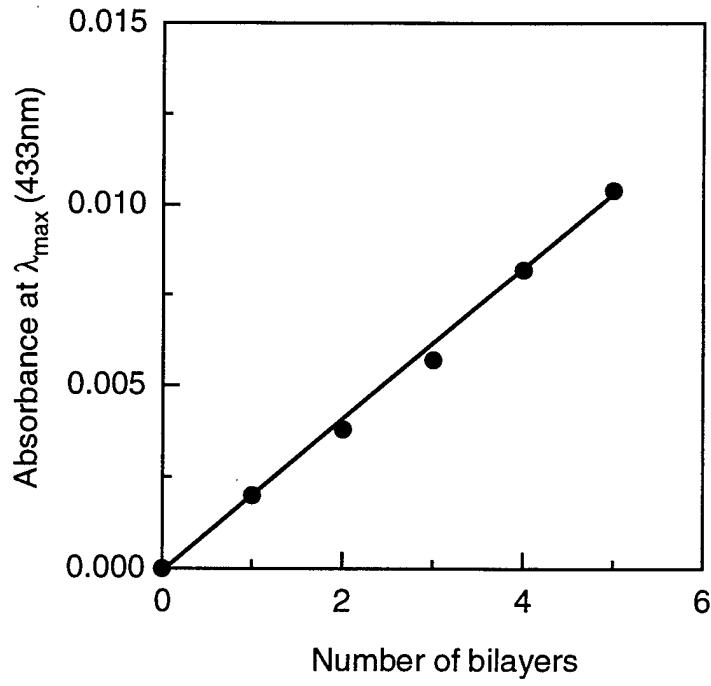


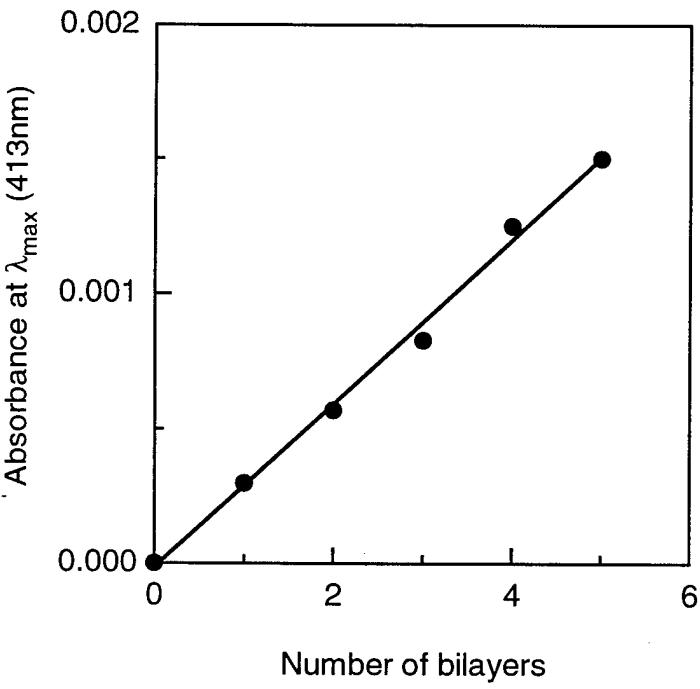
Fig. 2



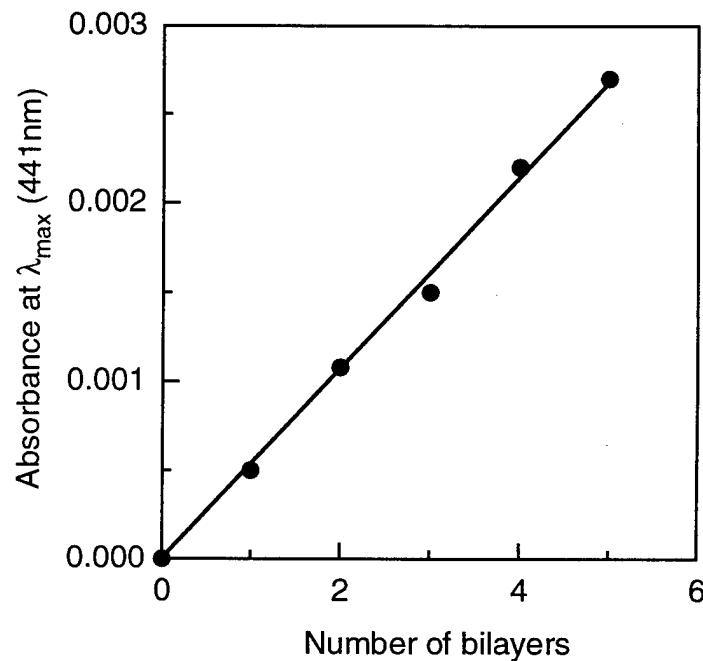
(a)



(b)



(c)



(d)

Fig. 3

Table 1. Properties of the polymers

| | M_n | M_w | polydispersity | T_d (°C) ^{b)} |
|-----|--------|---------|----------------|--------------------------|
| SIP | 62,800 | 114,800 | 1.83 | 422, 501 |
| SIT | 93,700 | 158,200 | 1.69 | 473 |
| PIP | 6,800 | 7,800 | 1.15 | 373, 478 |
| PIT | 6,800 | 7,900 | 1.16 | 441 |

^{a)} determined by GPC

^{b)} on-set decomposition temperature

Table 2. Absorption and fluorescence maxima of the polymers in water

| | Absorption (nm) | fluorescence (nm) ^{a)} |
|-----|-------------------------|---------------------------------|
| SIP | 455 (434) ^{b)} | - |
| SIT | 480 (465) | - |
| PIP | 373 (417) | 431 |
| PIT | 399 (444) | 457 |

^{a)} excited at each absorption maximum

^{b)} Numbers in the parentheses represent absorption maxima measured in DMF solution.